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008368742 **Image available**
WPI Acc No: 1990-255743/199034
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XRAM Acc No: C90-110695
XRPX Acc No: N90-198166

Suppressing hydrogen sulphide liberation in refinery residues - by addn. of diaminomethane(s), e.g. bis(dibutylamino), bis (morpholino)methane or bis (3-ME-piperidino)methane

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Inventor: WEERS J J
Number of Countries: 008 Number of Patents: 003
Patent Family:

Patent No	Kind	Date	Applicat No	Kind	Date	Week	
EP 383499	A	19900822	EP 90301407	A	19900209	199034	B
CA 2007965	A	19900813				199044	
CA 2007965	C	19960227	CA 2007965	A	19900117	199619	

Priority Applications (No Type Date): US 89310420 A 19890213
Cited Patents: 3.Jnl.Ref; A3...9040; DE 2651465; GB 2165753; NoSR.Pub; US 1719649; US 1771985; US 2496596; US 3025313; US 3094490; US 3236835; WO 8001570
Patent Details:

Patent No	Kind	Lan	Pg	Main IPC	Filing Notes
EP 383499	A				

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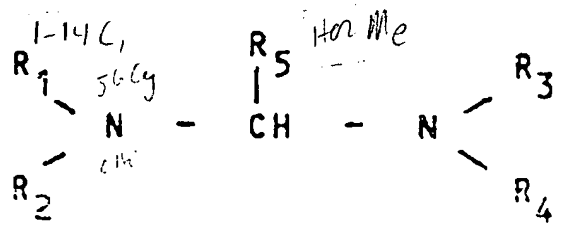
Patent No	Kind	Lan	Pg	Main IPC	Filing Notes
CA 2007965	C			C10G-029/20	

Abstract (Basic): EP 383499 A

Inhibition of H2S gas liberation during storage or transport of petroleum refinery residues is achieved by incorporation of a diaminomethane cpd of formula (I), where R1-4 = 1-14 (pref 1-9) C alkyl, 5- or 6-C cycloalkyl or -(CH2)nOR6 (n = integer 1-5 and R6 = 1-5 C alkyl), or R1 and R2 and/or R3 and R4 are alkylene gps forming N-heterocycles; and R5 = H or me.

USE/ADVANTAGE - (I) is effective at 10-10,000 (esp 100-1000) ppm in inhibiting H2S liberation from residues to be used as eg bunker or marine fuel oil. (7pp Dwg.No.0/0)



(I)

Title Terms: SUPPRESS; HYDROGEN; SULPHIDE; LIBERATING; REFINE; RESIDUE; ADD ; DI; AMINO; METHANE; DI; DI; MORPHOLINO; METHANE; DI; PIPERIDINO; METHANE
Derwent Class: E19; H06; Q49
International Patent Class (Main): C10G-029/20
International Patent Class (Additional): C10L-001/22; E21B-041/02
File Segment: CPI; EngPI
Manual Codes (CPI/A-N): E07-D05; E07-E03; E07-H04; E10-B01D; E10-B01E; H06-D07
Chemical Fragment Codes (M3):
01 F011 F012 F013 F014 F015 F016 F019 F021 F029 F433 F499 F553 F653

F699 F740 F799 G030 G039 G553 G563 G599 H1 H103 H181 H182 H201 H202
H581 H582 H583 H584 K0 L6 L640 L699 M126 M129 M143 M149 M210 M211
M212 M213 M214 M215 M216 M220 M221 M222 M223 M224 M225 M231 M232
M233 M240 M272 M273 M280 M281 M282 M283 M311 M312 M313 M314 M315
M321 M322 M323 M331 M332 M340 M342 M383 M391 M392 M393 M413 M415
M416 M510 M521 M522 M530 M540 M541 M542 M543 M620 M781 M903 M904
N101 Q412 9034-A9701-U 00245
Ring Index Numbers: 00245
Derwent Registry Numbers: 1785-U
Generic Compound Numbers: 9034-A9701-U

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Patents — Trade-marks — Copyright — Industrial design — Integrated circuit topography

(51) Int.Cl.[6] C10G 29/20

(19) (CA) **CANADIAN PATENT** (12)

(54) Suppression of the Evolution of Hydrogen Sulfide Gases from Petroleum Residua

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(73) Petrolite Corporation , U.S.A.

(30) (US) U.S.A. 310,420 1989/02/13

(57) 32 Claims

NO DRAWING

SUPPRESSION OF THE EVOLUTION OF HYDROGEN SULFIDE GASES FROM PETROLEUM RESIDUA

Field of the Invention

The present invention relates generally to the field of petroleum residua. More particularly, the invention relates to petroleum residua containing sulfur compounds capable of forming hydrogen sulfide gases.

Background of the Invention

A crude oil residuum or heavy oil which is often referred to as asphaltic fractions in the refining of crude oil is broadly understood to be the residue obtained from crude oil after a nondestructive distillation has removed substantially all of the volatile fractions. Refining temperatures are usually maintained below 350°C (660°F) as the rate of thermal decomposition of petroleum becomes substantial above such temperature. Residua are black, viscous materials and are obtained as a residue from atmospheric or vacuum distillation of a crude oil. They may be liquid at room temperature (generally atmospheric residua) or almost solid (generally vacuum residua) depending upon the crude oil. The organic chemical composition of residua are complex and may contain ash-forming metallic constituents and sulfur compounds, since metals and sulfur compounds of one type or another are generally present in crude oil. In residua, there are many varieties of sulfur compounds depending on the prevailing conditions during the formation thereof. The presence of

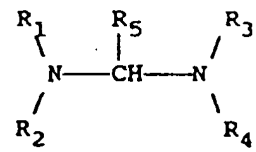
the sulfur compounds in the residua gives rise to the generation of a gas having substantial portions of hydrogen sulfide gas. Residua have found extensive use as a bunker fuel oil, No. 6 fuel oil, fuel oil C, and marine fuel oil. Residua must be transported from the refinery to the points of use, such as a ship or power generating plant. Unfortunately, during storage or such transport, hydrogen sulfide gases become liberated and give rise to a multitude of environmental problems.

Hydrogen sulfide is a very toxic gas and thus the use of residua requires special handling to ensure safety. The contamination of residua with hydrogen sulfide forming substances thus presents a series of problems as the residua are stored or transported. Providing an effective chemical method for suppressing or inhibiting the liberation of hydrogen sulfide gases from residua are of considerable importance. Methods heretofore known for suppressing the liberation of hydrogen sulfide gases from residua suffer from the standpoint of effectiveness.

Summary of the Invention

The present invention relates generally to petroleum residua containing hydrogen sulfide gas forming substances and to a method for chemically suppressing the liberation of the hydrogen sulfide gases from such residua. The suppression or inhibiting of the generation of the hydrogen sulfide gases is accomplished by incorporating into the residua at least one of the following diamine compounds in

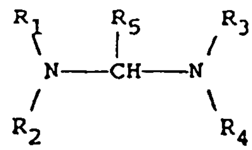
an amount sufficient to inhibit hydrogen sulfide gas evolution:



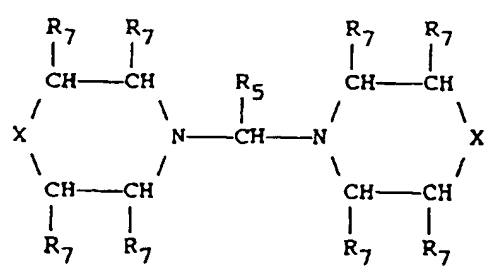
wherein R_1, R_2, R_3, and R_4 are each independently an alkyl radical containing 1 to 14 carbon atoms, $(CH_2)_n - OR_6$ or cycloalkyl containing 5 or 6 carbon atoms and R_5 is hydrogen or methyl. R_6 is an alkyl having 1 to 5 carbon atoms and n is an integer of 1 to 5. R_1 and R_2 or R_3 and R_4 or both can be joined to form a five or six member heterocyclic ring. Such ring can also include hetero atoms such as N, O, or S in addition to the N to which R_1 and R_2 and/or R_3 and R_4 are respectively joined. By including a diamine compound of the above general structure within residua in an amount of about 10 ppm to 10,000 ppm, it is possible to suppress satisfactorily the evolution of hydrogen sulfide gases which are normally generated during the storage and transfer of the residua. Preferably, the amount of diamine added to the residua ranges from about 100 ppm to about 1,000 ppm.

Detailed Description of the Invention

The composition of the present invention is generally comprised of petroleum residua and an effective amount of a diaminomethane having the following general structural formula:



wherein R_1, R_2, R_3, and R_4 are each independently an alkyl radical containing 1 to 14 carbon atoms, $(CH_2)_n-OR_6$ or cycloalkyl having 5 or 6 carbon atoms and R_5 is hydrogen or methyl. R_6 is an alkyl having 1 to 5 carbon atoms and n is an integer of 1 to 5. Additionally, R_1, R_2, R_3 and R_4 can be a lower alkylene wherein R_1 and R_2 alone and/or wherein R_3 and R_4, are joined together to form a five or six member saturated heterocyclic ring. Such ring can also contain hetero atoms such as N, O, or S in addition to the N to which R_1 and R_2 and/or R_3 and R_4 are respectively joined. The heterocyclic compounds of the present invention have the following structure.



where X is selected from the group of N, O, S or $-CR_8$ and R_5 is hydrogen or methyl and R_7 is hydrogen or C_1-C_4 alkyl and R_8 is hydrogen or C_1-C_4 alkyl. The diamine is incorporated in the residua after the residua are removed as a bottoms product from the refining of crude oil. The diamine should be thoroughly mixed in the residua. Thus, thorough incorporation of the diamine is preferably

accomplished while the residua are at a temperature sufficiently high for the residua to have a suitable mixing viscosity but at a temperature sufficiently low to prevent thermal degradation of the additive. Often residua are too viscous at room temperature for the diamine to be conveniently dispersed evenly throughout the residua. The incorporation of the additive to suppress the evolution of hydrogen sulfide gases should be made before the residua are stored or transported.

The diamines useful in the present invention can be prepared by reacting a suitable aldehyde and a suitable secondary amine or mixtures in a known and conventional manner. Thus, the diamines can be obtained by reacting a secondary amine typically having the formula:

$$R_1-\overset{\displaystyle R_2\atop\displaystyle |}{N}-H \quad \text{or} \quad R_3-\overset{\displaystyle R_4\atop\displaystyle |}{N}-H$$

in which R_1, R_2, R_3 and R_4 are as defined above with an aldehyde having the formula:

$$R_5-\overset{\displaystyle O\atop\displaystyle \|}{C}H$$

in which R_5 is as defined above. The secondary amine and the aldehyde are preferably combined in a mole ratio of about 2:1, i.e., the stoichiometric amount for the formation of diaminomethane with substantially no side products.

The diamines useful in the subject invention can be prepared under conventional dehydrating conditions whereby

water is removed by any suitable means. Typically, the aldehyde is added to the secondary amine and the condensate recovered by mechanically separating as much of the water of reaction as possible and distilling off the remaining water. The reaction is generally exothermic and the exotherm should be controlled particularly when the aldehyde is other than formaldehyde to prevent formation of enamines. The subject diamines can be formed from mixtures of different aldehydes and/or mixtures of different secondary amines.

The amount of the diamine as herein defined effective to inhibit hydrogen sulfide gas liberation will vary, depending on various factors, for example, the particular residuum and conditions of storage and transport. In practice, at least an amount of about 10 ppm additive based on the weight of the residuum is used and preferably an amount of at least 100 ppm is used. Amounts of diamine exceeding 10,000 ppm can be employed, but, in general, there is usually no commercial or technical advantage in doing so.

Test Procedure

In the following examples, the effectiveness of the diamine additive is determined by the following hydrogen sulfide gas evolution analysis. Into a metal container, the diamine additive and 500 grams of sample residua are charged at ambient temperature. After capping the container, the container and contents therein are heated in

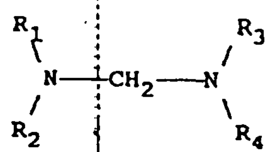
a constant temperature bath for 60 minutes at 180°F. The container is then removed from the bath and shaken in a shaker for 30 seconds. Thereafter, the container and contents are again heated at 180°F for another 30 minutes. After the first shaking operation, the container and the contents are shaken again for 30 seconds. Immediately, after the second shaking, the cap is replaced with a one hole stopper. Connected to the stopper hole is a Dräger tube whose other end is connected to a Dräger gas detector pump. With one stroke of the pump, a gas sample is withdrawn through the tube. The tube is removed from the container. Thereafter, two strokes of pure air are brought through the tube allowing the absorbed hydrogen sulfide to convert quantitatively. The length of the discoloration in the tube blackened by H_2S corresponds to the hydrogen sulfide concentration in the vapor above the liquid in the container. Alternatively, the headspace gas after the second shaking can be analyzed using a gas chromatograph connected to a mass spectrometer or other suitable device for quantitatively measuring H_2S.

In the following examples, all percentages are given on a weight basis unless otherwise indicated.

Example 1

Residuum from a large refining plant near St. Louis, Missouri, which is transported to a ship on the West Coast of the United States generates unacceptable quantities of hydrogen sulfide gas. The gas becomes an environmental

problem when the residuum is unloaded onto the ship. It is found that by adding an effective quantity (250 ppm) of a diamine having the following general formula the quantity of hydrogen gas emitted is substantially reduced:

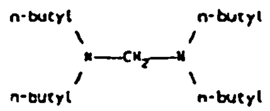
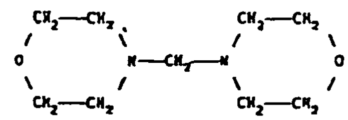
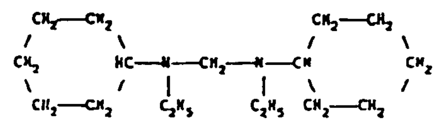
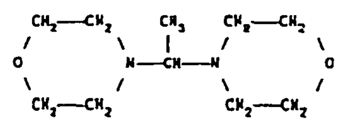
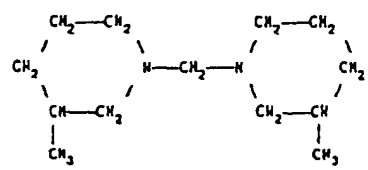


wherein each of R_1, R_2, R_3, and R_4 is n-butyl.

Example 2

In the laboratory, various diamines at additive levels of 100 ppm and 250 ppm were tested for their efficacy to suppress the liberation of hydrogen sulfide gas in residua using the above test procedure as above described. The residuum employed in the tests was a straight run residue from an atmospheric crude unit. The results of such tests have been summarized in the table on the following page:

Table

Test No.	Diaminomethane	Amount, ppm	H_2S in Head Space, ppm	% H_2S Reduction
1.	blank (no additive)	-	2500	-
2.		100	2196	12.2
		250	1521	39.9
3.		100	1489	40.4
		250	1347	46.1
4.		100	1687	32.5
		250	1293	48.3
5.		100	1378	44.9
		250	1030	58.8
6.		100	1291	48.4
		250	814	67.4

The diamine in Test No. 2 was obtained by heating two moles of dibutylamine to 80°C. One mole of formaldehyde in the form of 37% aqueous solution was then added dropwise. The resulting mixture was stirred at room temperature for 15 minutes. Thereafter, water was removed by evaporation. The product was identified as bis(dibutylamino)methane.

The diamine in Test No. 3 was obtained by heating two moles of morpholine to 80°C. One mole of formaldehyde in the form of a 37% aqueous solution was then added dropwise.

The resulting mixture was heated at 80°C for one hour. Thereafter, all water was distilled off leaving a clear oil product which was identified as bis(morpholino)methane.

The diamine of Test No. 4 was obtained by combining two moles of N-ethylcyclohexylamine and one mole of formaldehyde in the form of a 37% aqueous solution. The resulting mixture was stirred at room temperature for one hour and thereafter heated for one hour (at 80°C). Water was then distilled off. The product was identified as bis(N-ethylcyclohexylamino)methane.

The diamine of Test No. 5 was obtained as follows. Two moles of morpholine were cooled in ice and one mole of acetaldehyde was added dropwise to the cooled morpholine. The reaction was notably exothermic. After all the aldehyde had been added, the resulting mixture was stirred 15 minutes at room temperature. The mixture was subjected to rotary evaporation at room temperature and at 20mm H_g pressure to remove unreacted aldehyde and water. The resulting product was a viscous yellow oil and was identified as 1,1 bis(morpholino)ethane.

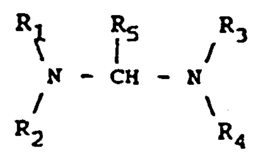
The diamine of Test No. 6 was prepared by heating two moles of 3-methylpiperidine and one mole of formaldehyde in the form of 37% aqueous solution with stirring at 80°C for 30 minutes. Water was then distilled off. The product was identified as bis(3-methylpiperidino)methane.

As various changes can be made in the above described invention without departing from the scope of the

invention, it is intended that the above description shall be interpreted as illustrative only and not in a limiting sense.

What is claimed is:

1. A process of inhibiting the liberation of hydrogen sulfide gas during storage or transport of petroleum residua containing dissolved hydrogen sulfide from a refinery comprising adding to said residua a sufficient amount of the following diaminomethane compound to inhibit hydrogen sulfide gas evolution:



wherein R_1, R_2, R_3, and R_4 are independently an alkyl radical containing one to 14 carbon atoms, $(CH_2)_n$-OR_6 or cycloalkyl having 5 or 6 carbon atoms or wherein R_1 and R_2 and/or R_3 and R_4 are alkylene groups joined together with their adjacent N to form a heterocyclic ring and wherein R_5 is hydrogen or methyl and R_6 is an alkyl having 1 to 5 carbon atoms and n is an integer of 1 to 5.

2. The process of claim 1 wherein the diamine is present in the amount of about 10 ppm to 10,000 ppm.

3. The process of claim 1 wherein each of R_1, R_2, R_3, and R_4 are alkyl radicals of 1 to 9 carbon atoms.

4. The process of claim 3 wherein the diamine is present in an amount of about 10 ppm to 10,000 ppm.

5. The process of claim 1 wherein each of the alkyl radicals are n-butyl radicals.

6. The process of claim 5 wherein the diamine is present in the amount of 10 ppm to 10,000 ppm.

7. The process of claim 1 wherein the diamine is present in the amount of 100 ppm to 1,000 ppm.

8. The process of claim 3 wherein the diamine is present in the amount of 100 ppm to 1,000 ppm.

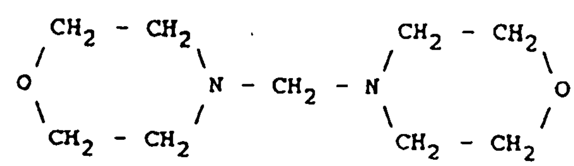
9. The process of claim 5 wherein the diamine is present in the amount of 100 ppm to 1,000 ppm.

10. The process of claim 1 wherein R_1 and R_2 and/or R_3 and R_4 are ethylene groups joined to form a heterocyclic structure having a hetero atom selected from the group consisting of N, O, or S in addition to the N to which R_1 and R_2 and/or R_3 and R_4 are respectively joined.

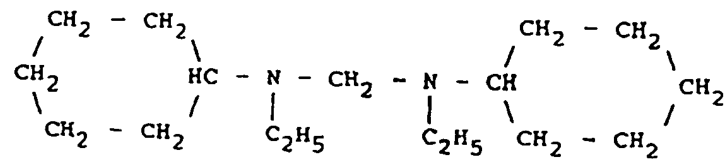
11. The process of claim 10 wherein the diamine is present in the amount of about 10 ppm to 10,000 ppm.

12. The process of claim 10 wherein the diamine is present in the amount of about 100 ppm to 1,000 ppm.

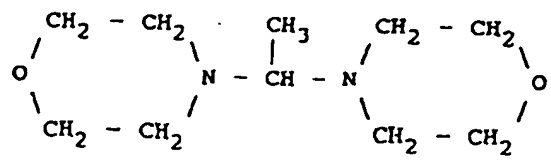
13. The process of claim 1 wherein the diamine has the chemical structure of



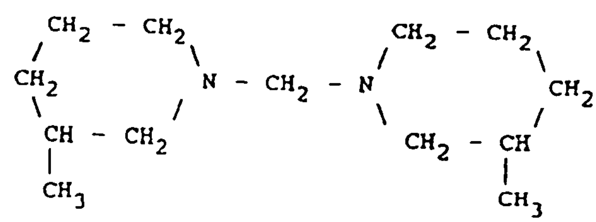
14. The process of claim 1 wherein the diamine has the chemical structure of



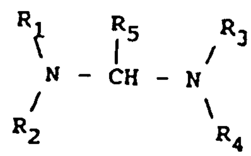
15. The process of claim 1 wherein the diamine has the chemical structure of



16. The process of claim 1 wherein the diamine has the chemical structure of



17. A composition comprising petroleum residua and a sufficient amount of the following diaminomethane compound to inhibit hydrogen sulfide gas liberation:



wherein R_1, R_2, R_3, and R_4 are independently an alkyl moiety containing 1 to 14 carbon atoms, $(CH_2)_n$-OR_6 or cycloalkyl having 5 or 6 carbon atoms or wherein R_1 and R_2 and/or R_3 and R_4 are alkylene groups joined together with their adjacent N to form a heterocyclic ring and R_5 is hydrogen or methyl and R_6 is an alkyl having 1 to 5 carbon atoms and n is an integer of 1 to 5.

18. The composition of claim 17 wherein the diamine is present in the amount of about 10 ppm to 10,000 ppm.

19. The composition of claim 17 wherein each of the alkyl moieties contain 1 to 9 carbon atoms.

20. The composition of claim 19 wherein the diamine is present in an amount of about 10 ppm to 10,000 ppm.

21. The composition of claim 17 wherein each of R_1, R_2, R_3, and R_4 are n-butyl radicals and R_5 is hydrogen.

22. The composition of claim 21 wherein the diamine is present in the amount of 10 ppm to 10,000 ppm.

23. The composition of claim 17 wherein the diamine is present in the amount of 100 ppm to 1,000 ppm.

24. The composition of claim 19 wherein the diamine is present in the amount of 100 ppm to 1,000 ppm.

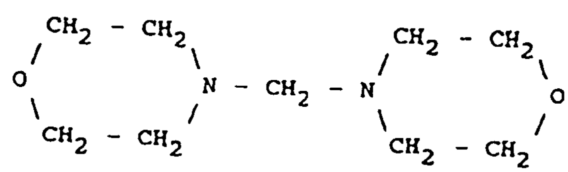
25. The composition of claim 21 wherein the diamine is present in the amount of 100 ppm to 1,000 ppm.

26. The composition of claim 17 wherein R_1 and R_2 and/or R_3 and R_4 are ethylene groups joined to form a heterocyclic structure having a hetero atom selected from the group consisting of N, O, or S in addition to the N to which R_1 and R_2 and/or R_3 and R_4 are respectively joined.

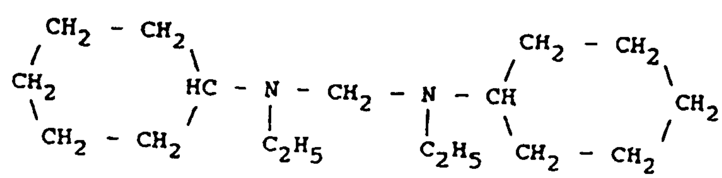
27. The composition of claim 26 wherein the diamine is present in the amount of about 10 ppm to 10,000 ppm.

28. The composition of claim 26 wherein the diamine is present in the amount of about 100 ppm to 1,000 ppm.

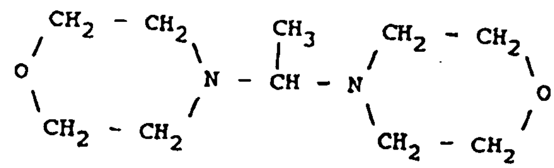
29. The composition of claim 17 wherein the diamine has the chemical structure of



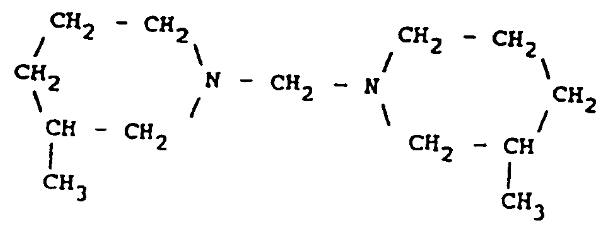
30. The composition of claim 17 wherein the diamine has the chemical structure of



31. The composition of claim 17 wherein the diamine has the chemical structure of



32. The composition of claim 17 wherein the diamine has the chemical structure of



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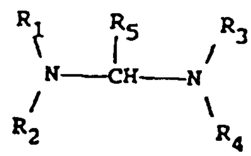
Abstract of the Disclosure

Hydrogen sulfide gas evolution during storage or transport of petroleum residua are suppressed by the incorporation of an effective amount of a diamine of the formula



wherein R_1, R_2, R_3, and R_4 are independently an alkyl radical containing 1 to 14 carbon atoms, $(CH_2)_n-OR_6$ or cycloalkyl containing 5 or 6 carbon atoms and R_5 is hydrogen or methyl. R_1 and R_2 and R_3 and R_4 can be alkylene groups joined together with their respective adjacent N to form a heterocyclic ring. R_6 is hydrogen or an alkyl radical having 1 to 5 carbon atoms and n is an integer of 1 to 5.